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Bioinspired Surface Treatments for Improved Decontamination: Fluoro-Plasma Treatment

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14. ABSTRACT

This effort evaluates bioinspired coatings for use in a top-coat type application to identify those technologies that may improve decontamination capabilities for painted surfaces. This report details results for evaluation of a plasma treatment developed at Edgewood Chemical Biological Center for the deposition of fluoropolymers. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphate, and diisopropyl fluorophosphates following treatment of contaminated surfaces with a soapy water solution is reported. Wetting behaviors for the treatment were also evaluated using sessile, sliding, and shedding contact angle measurements.

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EXECUTIVE SUMMARY

The Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) initiated a program in January 2015 for evaluation of bioinspired treatments suitable for use as a top coat on painted surfaces with the intention of achieving improved aqueous decontamination of these materials. Funding was provided by the Defense Threat Reduction Agency (DTRA, CB10125). This report details results for evaluation of a plasma treatment developed at Edgewood Chemical Biological Center for the deposition of fluoropolymers. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphate, and diisopropyl fluorophosphates following treatment of contaminated surfaces with a soapy water solution is reported along with droplet diffusion on the surfaces and wetting angles.

BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: FLUORO-PLASMA TREATMENT

INTRODUCTION

The DoD Chemical and Biological Defense Program (CBDP) seeks to provide protection of forces in a contaminated environment including contamination avoidance, individual protection, collective protection, and decontamination. In January 2015, the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) began an effort funded through the Defense Threat Reduction Agency (DTRA, CB10125) focused on the development and evaluation of top-coat type treatments suitable for application to painted surfaces. The goal of the effort was to identify approaches would reduce retention of chemical threat agents following standard decontamination approaches. The effort sought to survey relevant areas of research and evaluate identified technologies under appropriate methods to determine efficacy, scalability, and durability.

The current document summarizes results for one of the identified technologies. In this case, treated stainless steel coupons were provided to NRL by scientists at Edgewood Chemical Biological Center (ECBC; 07 Oct 2015). [1] The coupons incorporated a waterborne polyurethane paint system. Following application and curing, the paint was treated using a plasma deposition process for hexafluoroethane (C_2F_6) under 0.3 mbar vacuum. Variations included coupons treated at 50 W for 30 and 120 min as well as coupons treated at 75 W for 30 min (Figure 1). The coupons were subjected to the standard evaluations including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds.

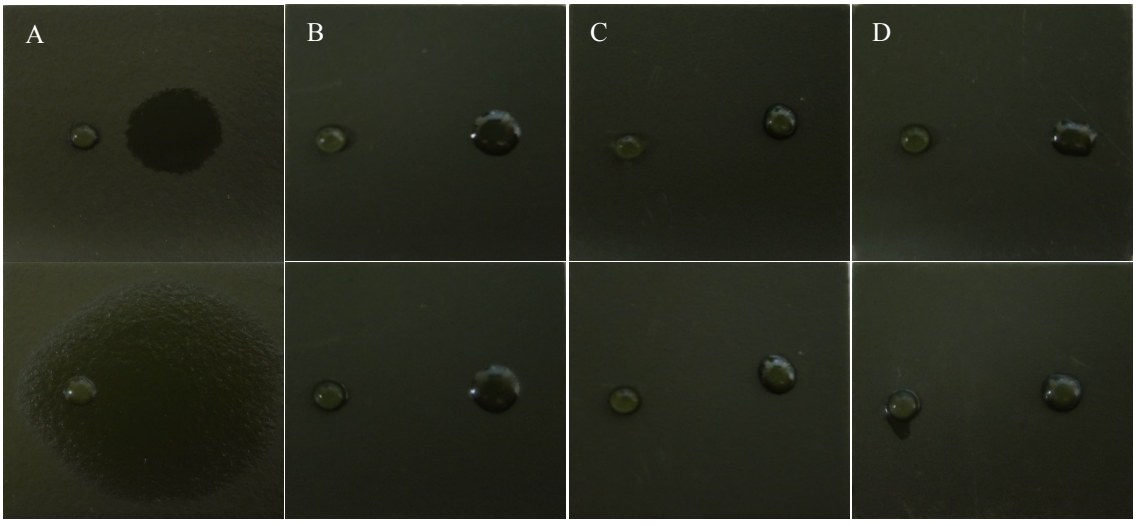

Fig. 1 — Images of a painted coupon and the three types of fluoro-plasma treated coupons with standing droplets of water (left) and methyl salicylate (right) immediately following liquid application (top) and 5 min after liquid application (bottom): painted coupon (A), C_2F_6, 50 W, 30 min (B), C_2F_6, 75 W, 30 min (C), C_2F_6, 50 W, 120 min (D).

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METHODS

Sessile contact angles for samples evaluated under this effort used three 3 μL droplets per surface with each droplet measured independently three times for water, ethylene glycol, and n-heptane. Geometric surface energy was calculated based on the water and ethylene glycol interactions using software designed for the DROPimage goniometer package. Sliding angles were determined using 5 μL droplets. The droplet was applied at 0° after which the supporting platform angle was gradually increased up to 60°. Sliding angles for each of the liquids were identified as the angle for which movement of the droplet was identified. Shedding angles for each liquid were determined using 12 μL droplets initiated 2.5 cm above the coupon surface. Changes in base angle of 10° were utilized to identify the range of droplet shedding angle based on a complete lack of droplet retention by the surface (not sliding). The angle was then reduced in steps of 1° to identify the minimum required angle. Coupons were equilibrated to a particular relative humidity by holding a previously dried sample (100°C) under the relevant humidity at 24°C for 48 h. Humidity controlled through the use of saturated salt solutions. Droplet diameters were determined using tools provided by Adobe Photoshop CS3. Droplets of 5 mL were applied to the surfaces and images were collected at 30 s intervals for 5 min followed by images at 5 min intervals for a total of 30 min. DFP samples were kept covered for the duration of the experiment to minimize evaporation. In some cases, reflections from the glass cover can be seen in the images.

Simulant exposure and evaluation methods were based on the tests developed by Edgewood Chemical Biological Center referred to as Chemical Agent Resistance Method (CARM). [2] Standard target exposures utilized a challenge level of 10 g/m^2. The coupons provided by ECBC were 0.000645 m^2; the 10 g/m^2 target challenge was applied to the surfaces as a single neat droplet: 5.1 μL paraoxon; 5.5 μL MES; 5.6 μL DMMP; 6.1 μL DFP. Following application of the target, coupons were aged 5 min or 1 h prior to rinsing with a low pressure stream of water (deionized). The coupons were then soaked in isopropanol for 30 min to extract remaining target; this isopropanol extract was analyzed by the appropriate chromatography method to determine target retention on the surface. An alternative method used a gentle stream of air to expel target from the surface prior to rising with soapy water (0.59 g/L Alconox in deionized water). An additional point of comparison was collected in which samples were subjected to the above protocol with no rinse step. Direct extraction in isopropanol was intended to provide the maximum target that could be expected to be recovered from the coupons.

For paraoxon analysis, a Shimadzu High Performance Liquid Chromatography (HPLC) system with dual-plunger parallel flow solvent delivery modules (LC-20AD) and an auto-sampler (SIL-20AC; 40 μL injection volume) coupled to a photodiode array detector (SPD-M20A; 277 nm) was used. The stationary phase was a C18 stainless steel analytical column (Luna, 150 mm x 4.6 mm, 3 μm diameter; Phenomenex, Torrance, CA) with an isocratic 45:55 acetonitrile: 1% aqueous acetic acid mobile phase (1.2 mL/min). [3] For analysis of methyl salicylate (MES), diisopropyl fluorophosphates (DFP), and dimethyl methylphosphonate (DMMP), gas chromatography-mass spectrometry (GC-MS) was accomplished using a Shimadzu GCMS-QP2010 with AOC-20 auto-injector equipped with a Restex Rtx-5 (30 m x 0.25 mm ID x 0.25 μm df) cross bond 5% diphenyl 95% dimethyl polysiloxane column. A GC injection temperature of 200°C was used with a 1:1 split ratio at a flow rate of 3.6 mL/min at 69.4 kPa. The oven gradient ramped from 50°C (1 min hold time) to 180°C at 15°C/min and then to 300°C at 20°C/min where it was held for 5 min.

RESULTS

Analysis of the painted surfaces alone provides a point of comparison for evaluating the benefits of the surface treatments. Table 1 provides contact angles collected for coupons coated with the polyurethane paint system only. As shown, the plasma treatments significantly increased the wetting angles for both water and ethylene glycol. Heptane wetted all surfaces, producing contact angles below the measurable threshold. Water contact angles are below those typically considered superhydrophobic (or ultrahydrophobic, >150°); however, geometric surface energies were reduced by up to an order of magnitude. The surfaces did not produce sliding or shedding for the test liquids with the exception of water on the C_2F_6, 50 W, 120 min surface. On this surface, an angle of 35° was determined for water shedding and sliding. During collection of the replicates in this dataset, some increase in contact angle variability was noted following rinsing with water and drying. As a result, an experiment was completed in which the surfaces were baked at 100°C or equilibrated to a specific relative humidity prior to collection of contact angles (Table 2). The impact of surface humidification was most pronounced for the C_2F_6, 50 W, 30 min sample, and very little impact was noted for the C_2F_6, 50 W, 120 min sample.

Table 1 – Sessile, Sliding, and Shedding Contact Angles

Coupon	Liquid	Sessile Angle	Sliding Angle	Shedding Angle	Geometric Surface Energy (mJ/m^2)
Paint Only	water	47.5 ± 1.1	>60	>60	71.9 ± 5.1
	ethylene glycol	55.7 ± 2.1	>60	>60	
	n-heptane	--	>60	>60	
C_2F_6, 50 W, 30 min	water	119.2 ± 2.6	>60	>60	7.1 ± 1.5
	ethylene glycol	105.3 ± 1.6	>60	>60	
	n-heptane	--	>60	>60	
C_2F_6, 75W, 30 min	water	123.5 ± 1.2	>60	>60	15.5 ± 2.0
	ethylene glycol	100.1 ± 1.0	>60	>60	
	n-heptane	--	>60	>60	
C_2F_6, 50 W, 120 min	water	137.1 ± 2.0	35 ± 3.0	35 ± 2.0	14.0 ± 2.6
	ethylene glycol	111.8 ± 1.2	>60	>60	
	n-heptane	--	>60	>60	

The tendency of droplets to spread across the surfaces was also evaluated (Figure 2; Appendix A). For these studies, droplets of the simulants (5 μL) were utilized. The spread of the droplets was quantified by measuring the diameter of the droplets in the images over time (Figure 3). For the paint only samples, MES and DFP spread quickly reaching the edges of the coupon at 10 and 2 min, respectively. DMMP does not spread during the course of the 30 min incubation. Similarly, for the plasma treatments, there is little spread of either DMMP or MES over the 30 min incubation. DFP, on the other hand, behaves differently on the different treatments. The spread of DFP is slowed on the C2F6, 50 W, 30 min and C2F6, 75 W, 30 min, but it does continue to spread until the surface is fully covered. On the C2F6, 50 W, 120 min surface, however, DFP does not spread.

Table 2 – Sessile Contact Angles Following Equilibration at Differing Relative Humidity

Coupon	%RH	Water Angle	Ethylene Glycol Angle	Geometric Surface Energy (mJ/m^2)
C2F6, 50 W, 30 min	0	127.8 ± 0.5	113.6 ± 1.1	5.5 ± 0.8
	33	122.9 ± 1.1	110.5 ± 1.2	5.7 ± 0.8
	53	130.0 ± 0.3	113.7 ± 1.2	6.6 ± 0.9
	84	127.9 ± 1.3	110.2 ± 1.4	8.2 ± 1.7
C2F6, 75 W, 30 min	0	126.1 ± 0.5	110.3 ± 1.8	7.3 ± 1.3
	33	124.9 ± 1.0	106.9 ± 1.2	9.2 ± 1.4
	53	129.8 ± 1.9	104.6 ± 0.4	16.1 ± 2.4
	84	129.2 ± 0.4	109.1 ± 0.8	10.0 ± 0.9
C2F6, 50 W, 120 min	0	129.2 ± 1.4	119.4 ± 0.3	3.3 ± 0.3
	33	126.6 ± 1.8	110.4 ± 0.7	7.2 ± 1.0
	53	130.1 ± 0.7	118.2 ± 0.6	4.4 ± 0.5
	84	132.7 ± 1.0	114.4 ± 1.0	7.6 ± 1.2

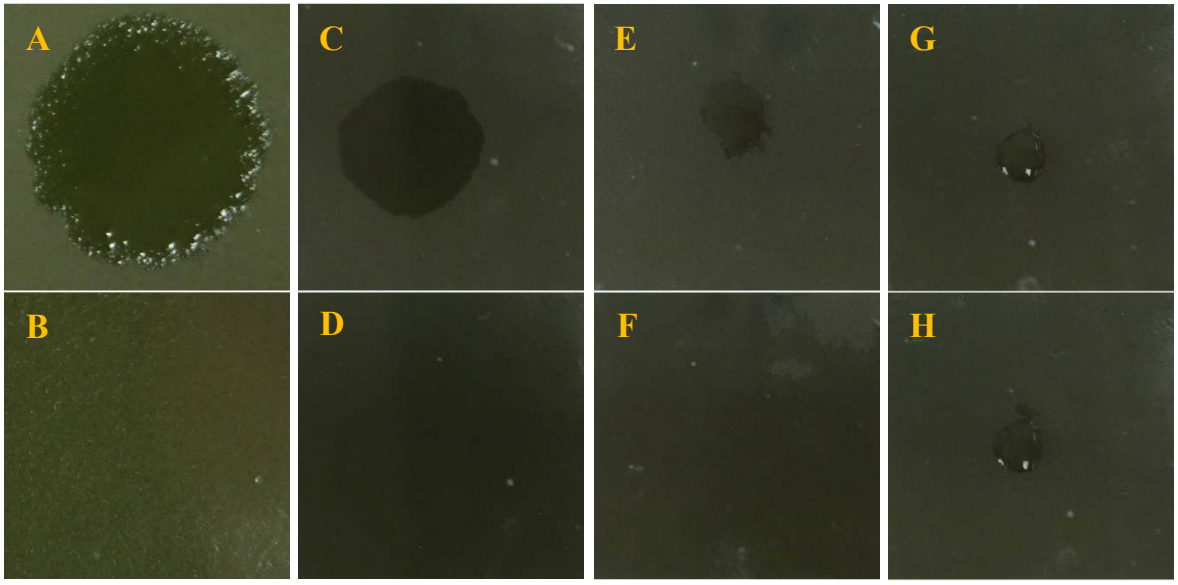

Fig. 2 — Images of a painted coupon and painted coupons treated with the plasma formulations with standing droplets of DFP: painted coupon with DFP immediately following application (A) and at 30 min (B); C2F6, 50 W, 30 min with DFP immediately following application (C) and at 30 min (D); C2F6, 75 W, 30 min with DFP immediately following application (E) and at 30 min (F); and C2F6, 50 W, 120 min with DFP immediately following application (G) and at 30 min (H).

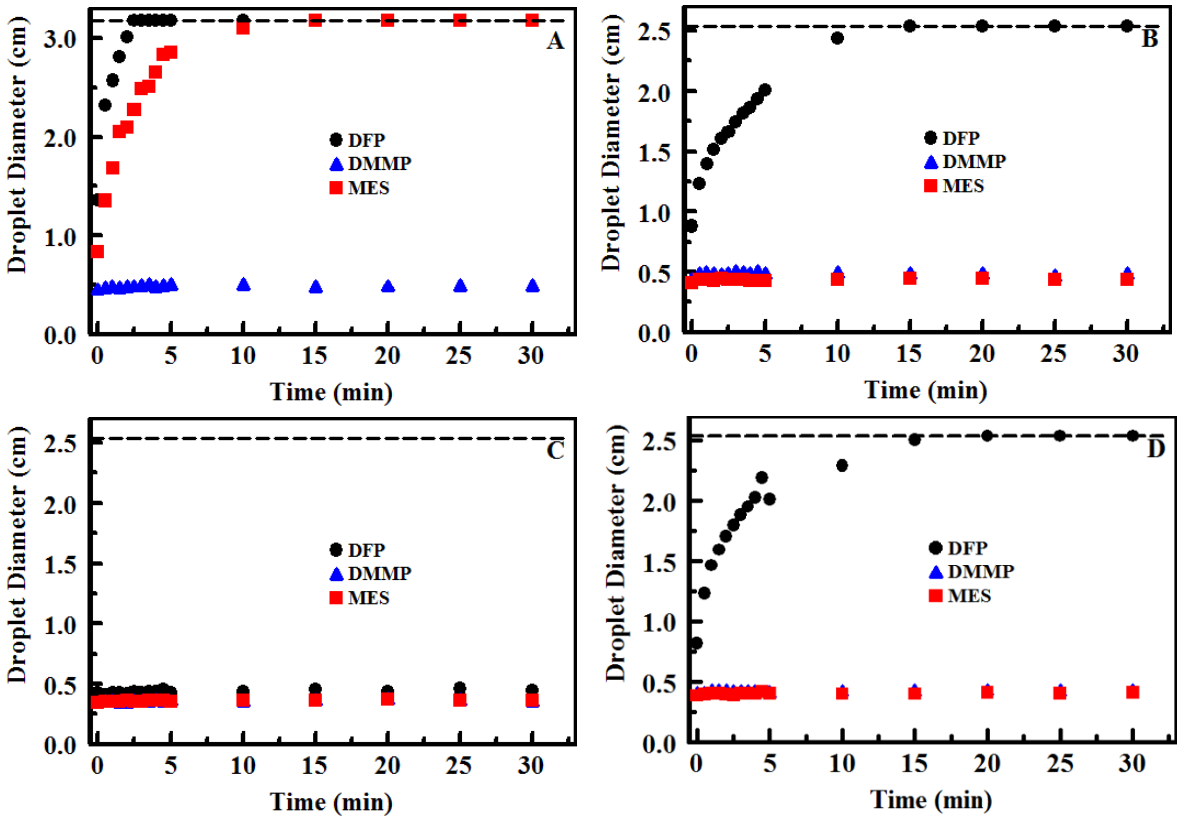

Fig. 3 — Progression of simulant droplet diameters during incubation on the surfaces for DFP (black), DMMP (blue), and MES (red): paint only (A), C2F6, 50 W, 30 min (B), C2F6, 50 W, 120 min (C), C2F6, 75 W, 30 min (D).

The coupons were subjected to several cycles of simulant exposure, aging, washing, and drying over a period of two weeks. No significant changes in the appearance or wetting characteristics were noted during this period. When the soapy water process was employed (Figure 2; Table 3), retention of all targets was significantly reduced by the plasma treatment process. Retained DMMP was below the detection threshold for that compound for all plasma treated coupons. DFP retained by the plasma treated coupons was less than 1% of that applied. Paraoxon and MES retention were less than 12% of the applied target.

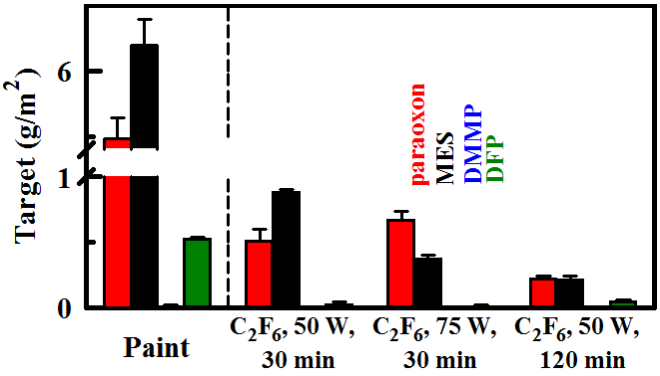

Fig. 4 — Target retention by coupons following treatment with an air stream followed by rinsing with soapy water.

Table 3 – Target Retention (g/m^2) Following 1 h Aging

Coupon	Target	No Rinse	Water Only	Air & Soapy Water
Paint Only	paraoxon	9.84	8.69	5.48
	MES	9.54		6.20
	DMMP	9.90		4.28
	DFP	7.39	0.79	0.52
C2F6, 50 W, 30 min	paraoxon	9.62	1.32	0.51
	MES	9.54	1.63	0.88
	DMMP	8.55	ND	ND
	DFP	6.23	1.16	0.02
C2F6, 75W, 30 min	paraoxon	9.65	1.99	0.67
	MES	8.79	0.50	0.37
	DMMP	9.65	ND	ND
	DFP	8.04	0.67	ND
C2F5, 50 W, 120 min	paraoxon	9.86	1.82	0.22
	MES	9.45	0.91	0.21
	DMMP	8.32	ND	ND
	DFP	7.23	0.60	0.04

ND = not detected

Table 3 presents additional results for coupons that were not rinsed prior to isopropanol extraction and for coupons rinsed with water only. Though the nominal target application was 10 g/m^2, recovery from surfaces was always less than this value. Losses due to evaporation would be expected, especially for DFP. Additional losses likely occur during the rinse steps due to agent interaction with the untreated region of the coupon; the back of these coupons is unpainted stainless steel. Target retention following soapy water rinse was always less than that noted for water only rinse.

CONCLUSIONS

The surface treatment considered here provides low surface energy as well as low target retention in both simulant and agent studies. [1] Results are similar to those of the most effective treatments evaluated under this effort. These results point to potential for the development of a coating that meets the needs for improved decontamination. Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. The long term stability of the coatings also needs to be more thoroughly evaluated.

One additional point needs to be mentioned, based on work by B. Mantooth (ECBC), it is possible that the performance change for these materials versus typical polyurethane coatings is not related to the perfluoroalkane treatment. An unintentional discovery related to use of an ionization source indicates that similar changes may be achieved by placing painted surfaces in the presence of ionizing radiation. These considerations need to be evaluated further.

ACKNOWLEDGMENTS

The comments of Dr. Brent Mantooth (ECBC) on methods and agent analysis are appreciated. This research was sponsored by the Defense Threat Reduction Agency (DTRA, CB10125).

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3. Y.T. Gebreegzi; G.D. Foster; S.U. Khan, "Simulltaneous Determination of Carbaryl, Malathion, Fenitrothion, and Diazinon Residues in Sesame Seeds (*Seasmum indicum* L) " *J. Agric. Food Chem.* **48**, 5165-5168 (2000).

Appendix

COUPON IMAGES

Fig. A1 — DFP on the C2F6, 50 W, 30 min treatment (1" x 1" coupon). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

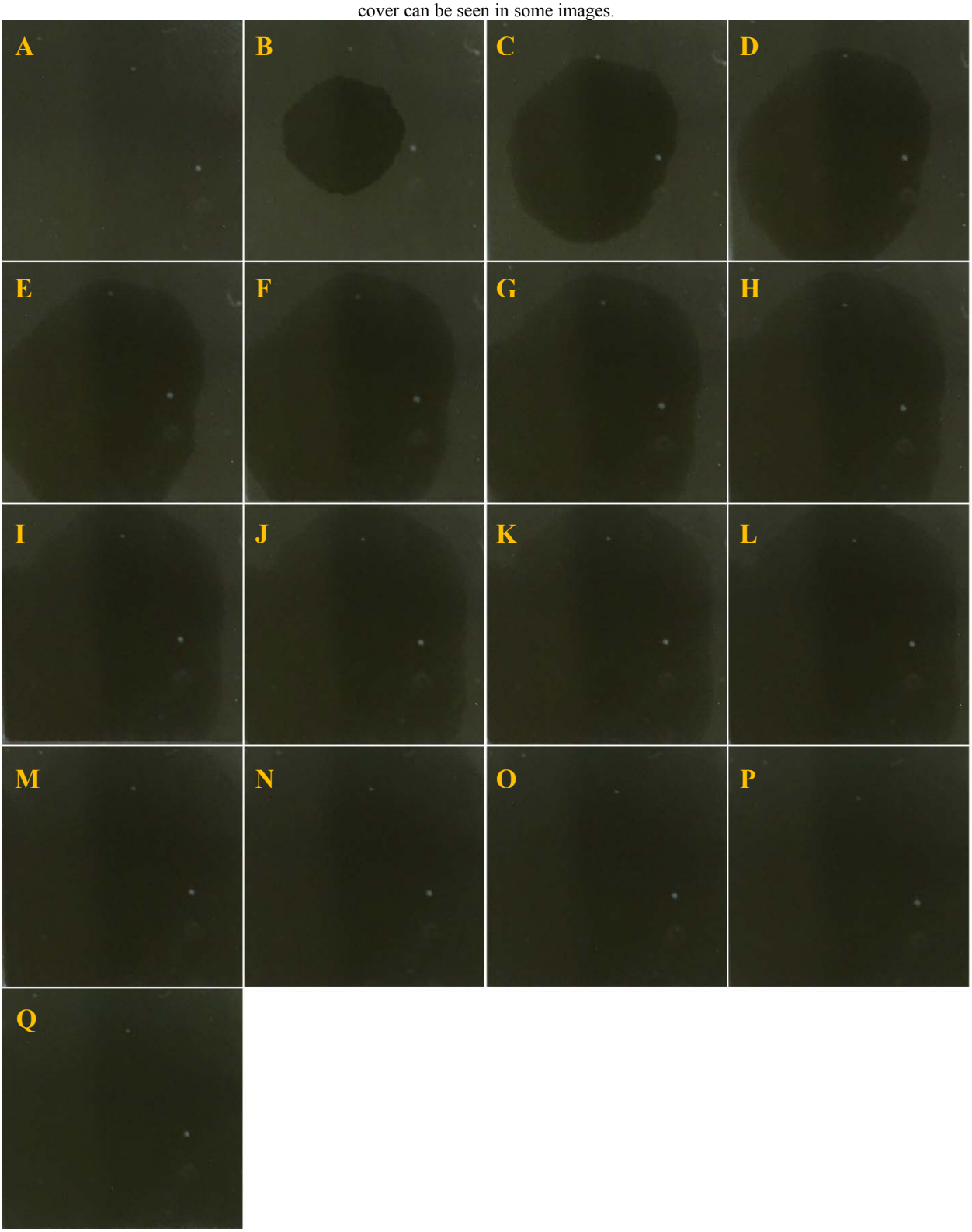

Fig. A2 — MES on the C2F6, 50 W, 30 min treatment (1" x 1" coupon). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

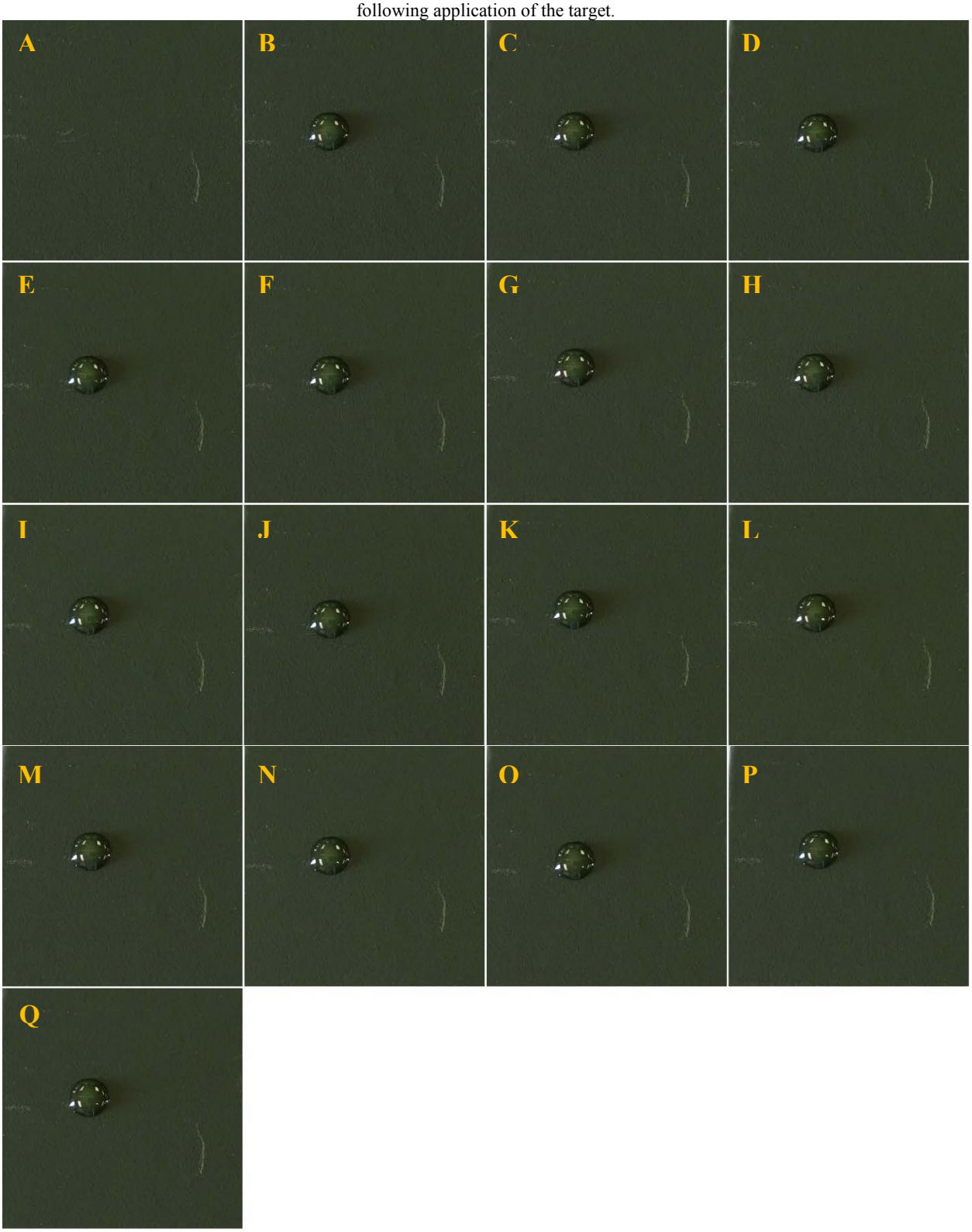

Fig. A3 — DMMP on the C2F6, 50 W, 30 min treatment (1" x 1" coupon). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

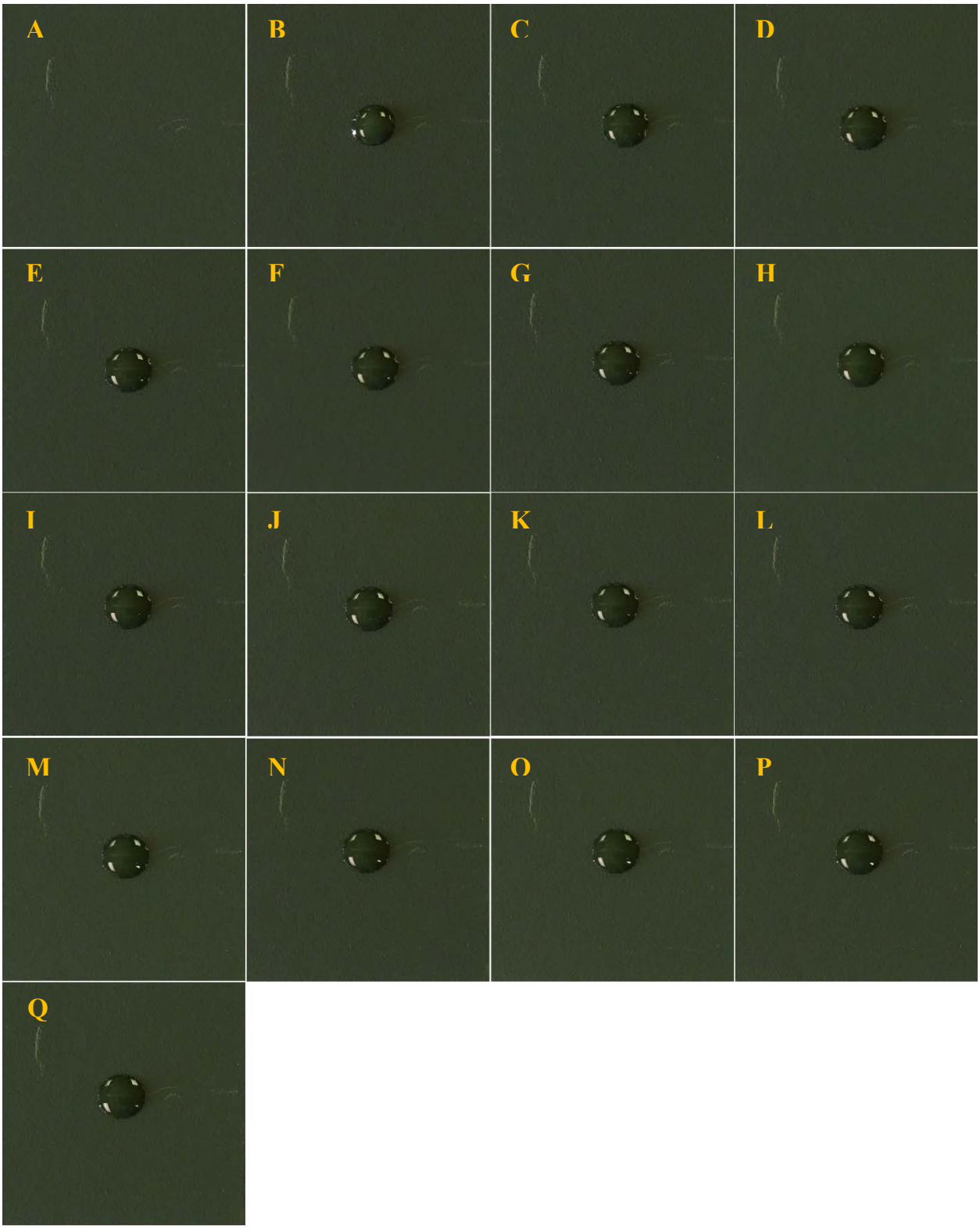

Fig. A4 — DFP on the C2F6, 75 W, 30 min treatment (1" x 1" coupon). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

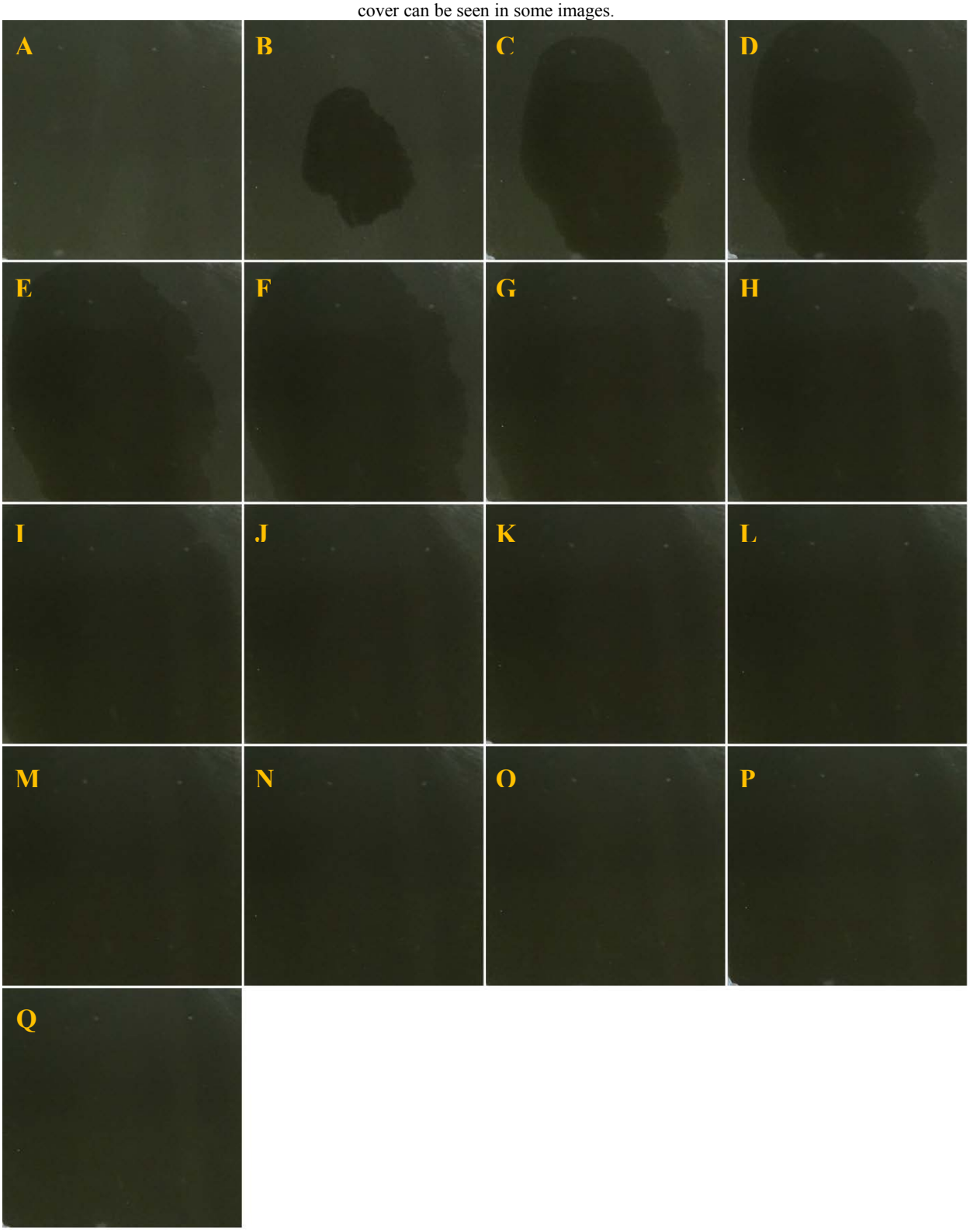

Fig. A5 — MES on the C2F6, 75 W, 30 min treatment (1" x 1" coupon). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

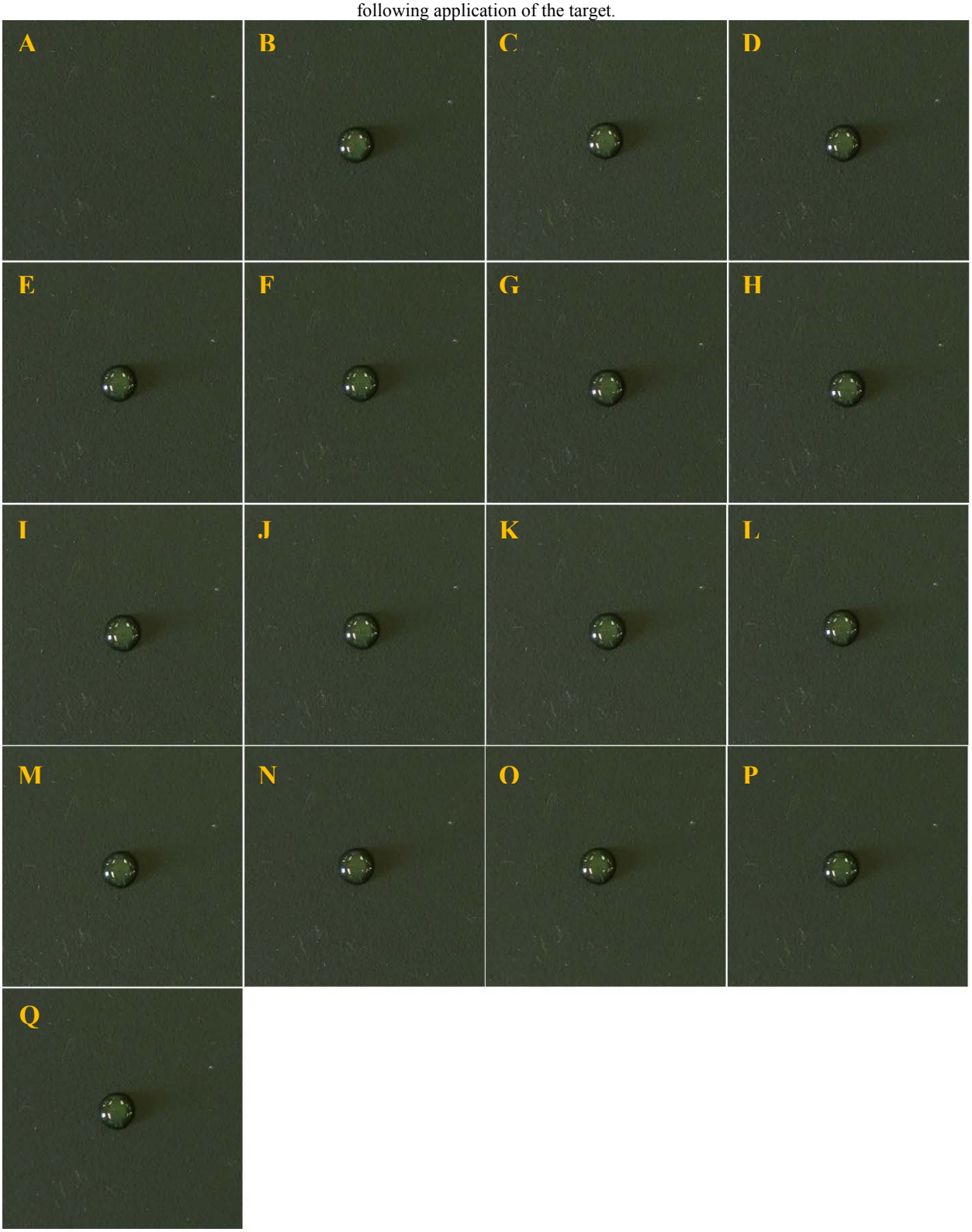

Fig. A6 — DMMP on the C2F6, 75 W, 30 min treatment. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

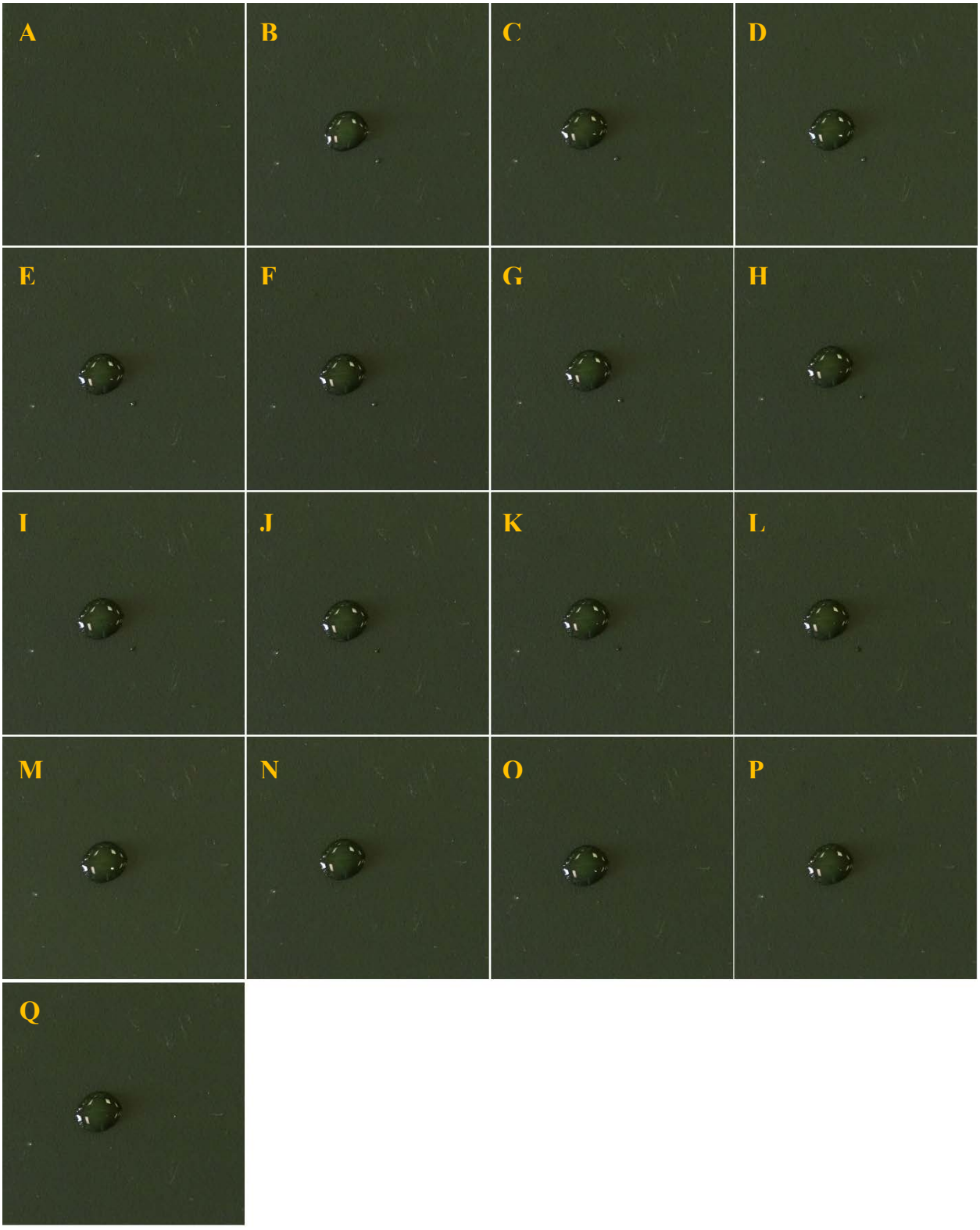

Fig. A7 — DFP on the C2F6, 50 W, 120 min treatment (1" x 1" coupon). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

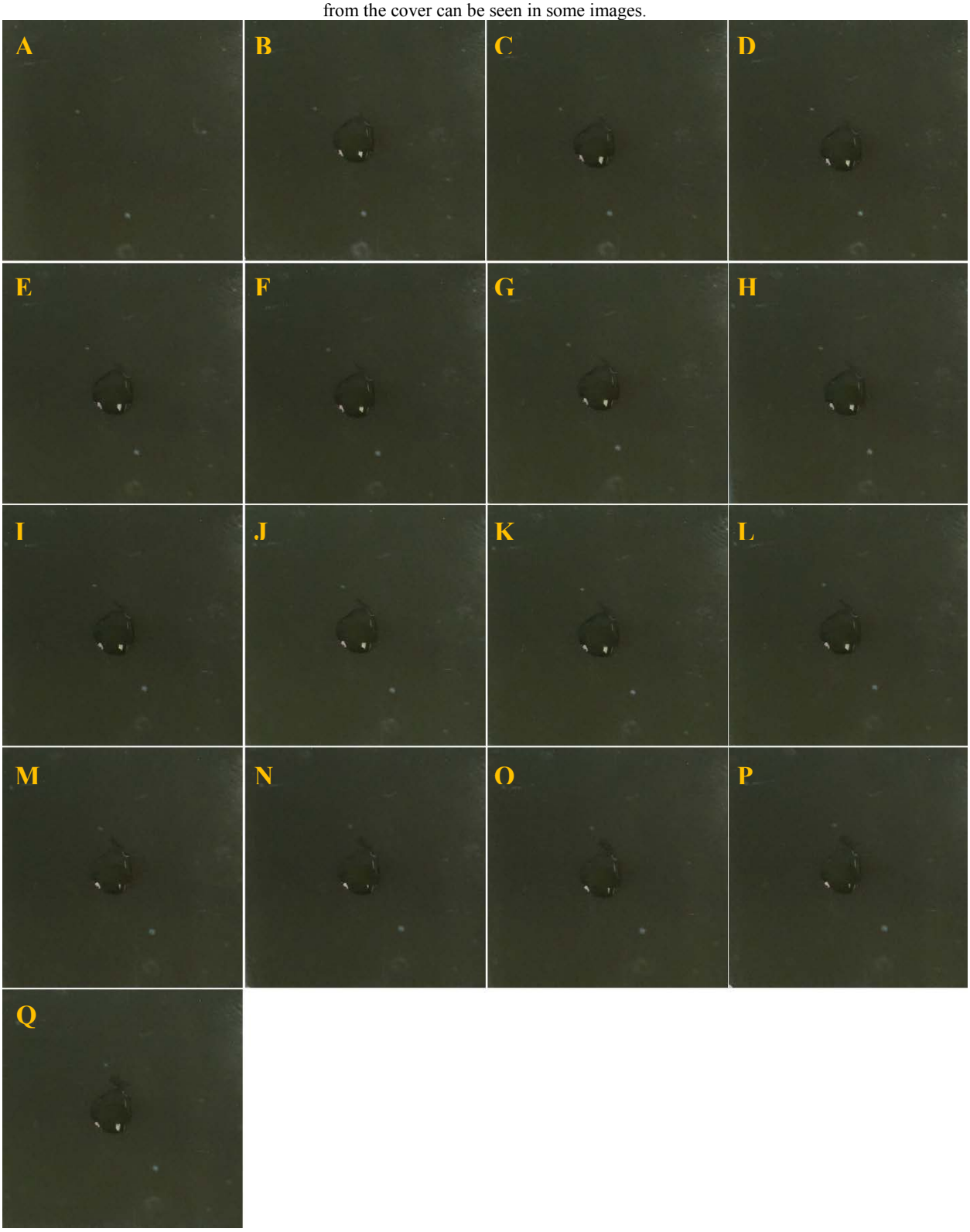

Fig. A8 — MES on the C2F6, 50 W, 120 min treatment (1" x 1" coupon). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

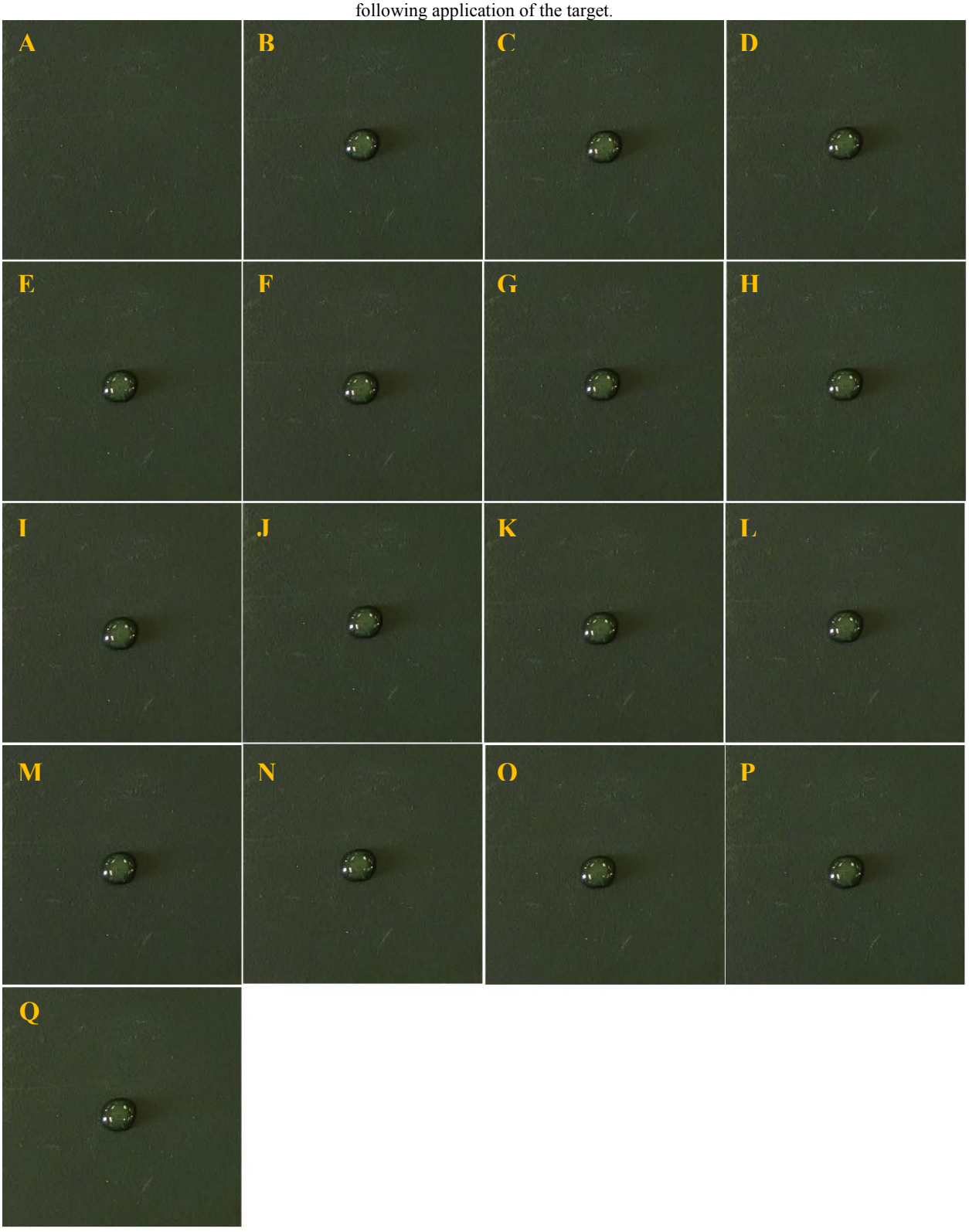

Fig. A9 — DMMP on the C2F6, 50 W, 120 min treatment (1" x 1" coupon). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.